

- [54] **PRODUCTION OF FERTILIZERS**
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- [58] Field of Search..... C05b/7/00; 71/34, 71/37, 40, 41, 39; 23/107, 165, 165 C, 312 P, 90, 109; 423/309, 308, 312, 313

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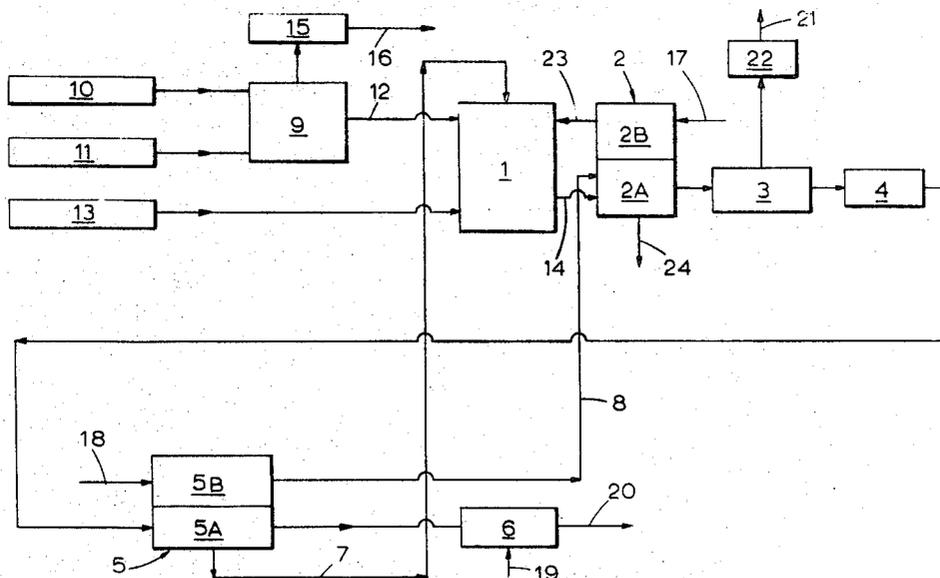
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[57] **ABSTRACT**

The invention relates to the production of fertilizers, in particular potassium dihydrogen phosphate. This is obtained through acid attack on phosphate rock by a medium obtained by the reaction of sulphuric acid with potassium chloride. In particular, the phosphate rock is reacted with a medium comprising potassium bisulphate, sulphuric acid and phosphoric acid. As a result, the solid calcium sulphate formed in the reaction mixture can be readily filtered off from the mother liquor and the potassium dihydrogen phosphate product can be recovered in a commercially operative process. The mother liquor containing phosphoric acid and potassium dihydrogen phosphate is recycled to the original reaction mixture.

22 Claims, 4 Drawing Figures



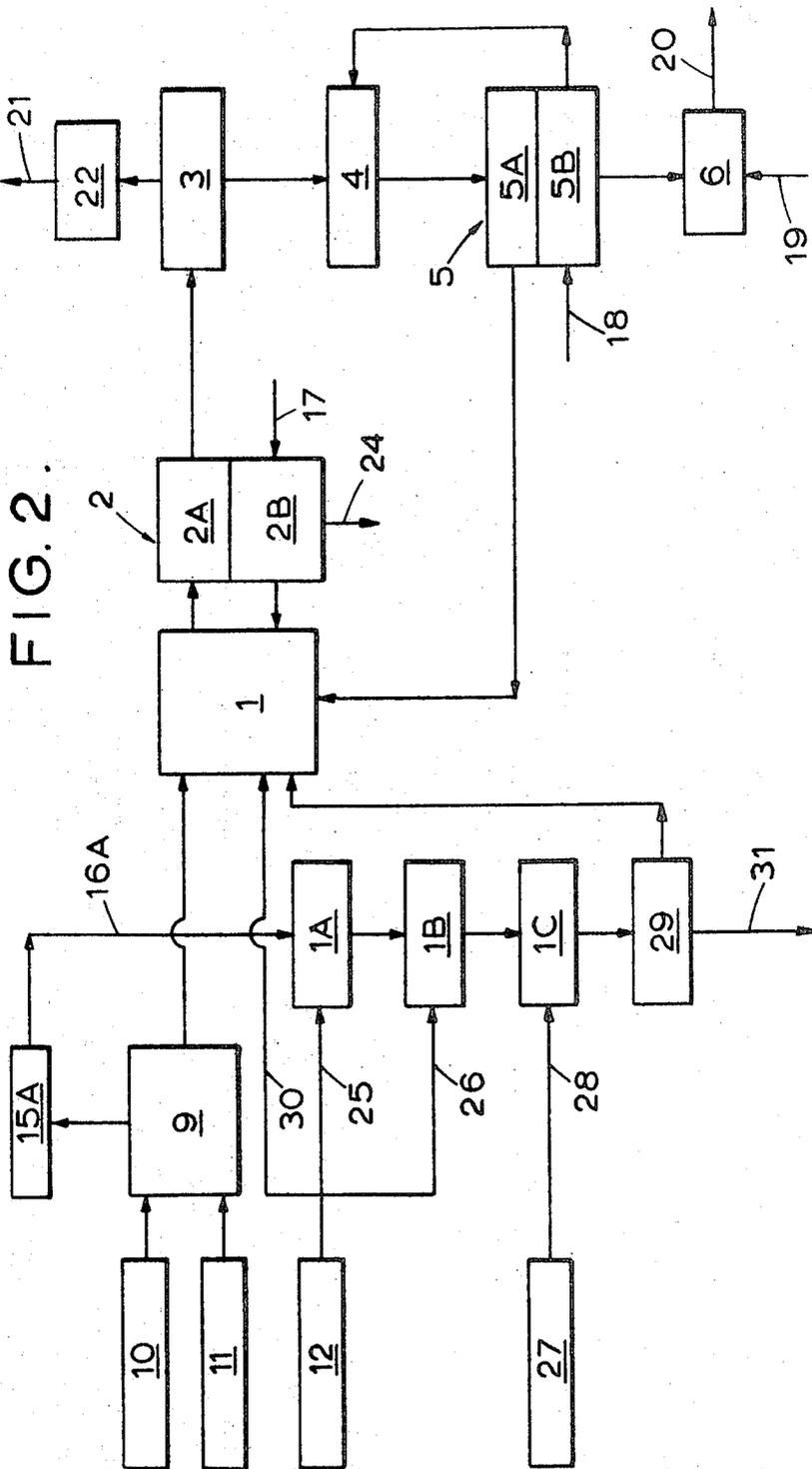


FIG. 2.

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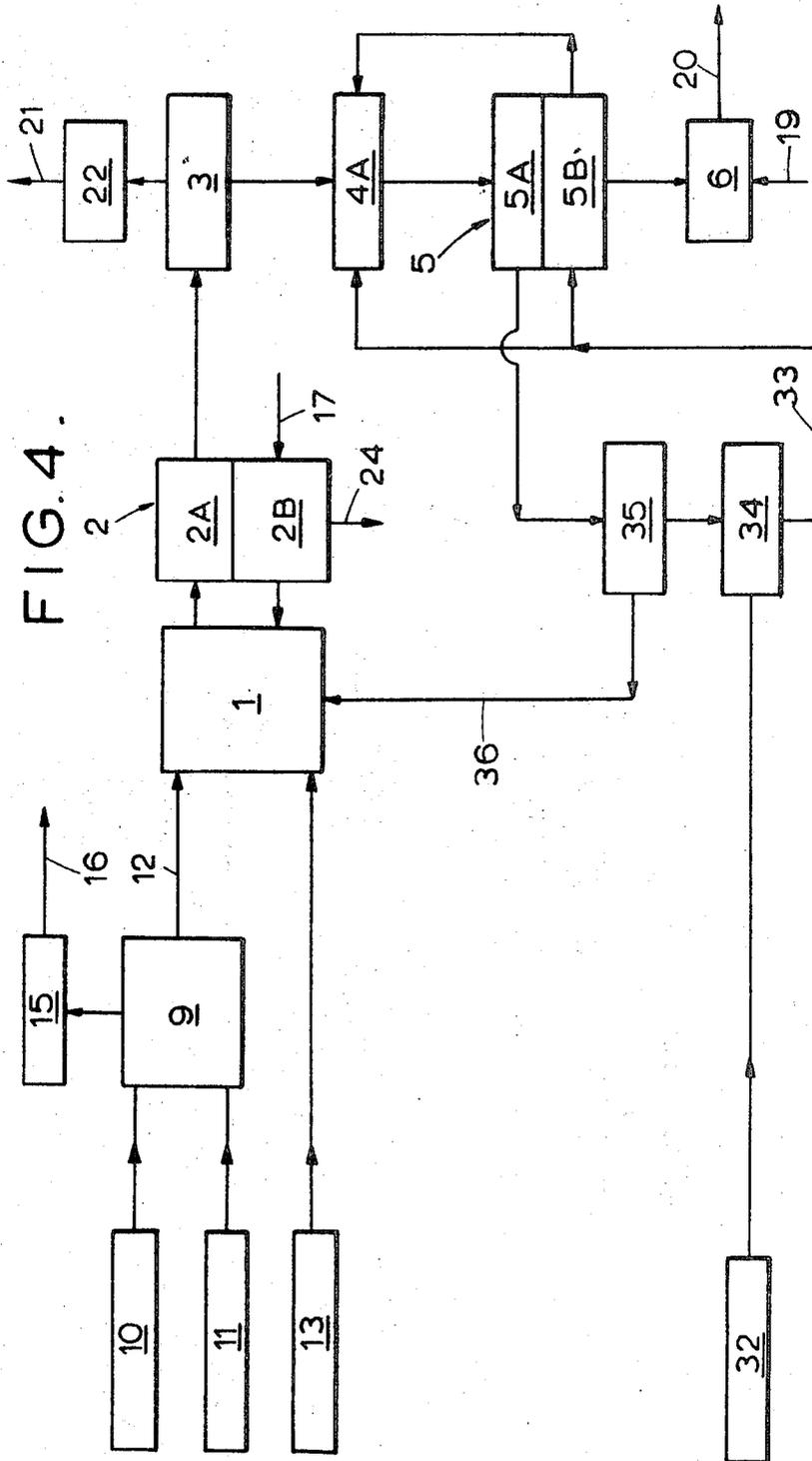


FIG. 4.

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PRODUCTION OF FERTILIZERS

This application is a continuation-in-part of my co-pending application Ser. No. 859,435, filed Sept. 19, 1969.

This invention relates to the production of fertilizers and is particularly concerned with the production of potassium dihydrogen phosphate which is particularly valuable in presenting both potassium and phosphorus in a convenient solid form which can be used either as a fertilizer directly or in combination with other components.

We propose to obtain potassium dihydrogen phosphate through acid attack on phosphate rock.

Accordingly, in this invention, we provide a process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with an aqueous medium containing potassium bisulphate, sulphuric acid and phosphoric acid to form a reaction mixture containing said potassium dihydrogen phosphate; controlling in said reaction mixture the weight percentages of hydrogen (other than in water) and of sulphate ion (in solution) relatively to phosphorus pentoxide to ensure precipitation of calcium sulphate in a readily separable state; and separating said calcium sulphate from said reaction mixture, whereby said potassium dihydrogen phosphate is recoverable from said reaction mixture.

In general, the H/P₂O₅ weight percentage is greater than about 2 percent and the SO₄/P₂O₅ weight percentage is greater than about 3 percent. Preferably, the H/P₂O₅ weight percentage is greater than about 3 percent, e.g. about 4 percent, and the SO₄/P₂O₅ weight percentage is greater than about 5 percent, e.g. about 6 to 7 percent.

The attacking medium may be formed through the reaction of sulphuric acid on potassium chloride.

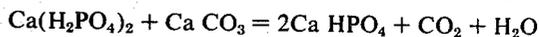
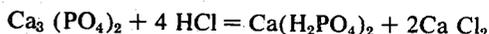
The solid calcium sulphate as dihydrate, hemi hydrate or anhydrite formed in the reaction mixture can be readily filtered off from the mother liquor, and the potassium dihydrogen phosphate product can be recovered in a commercially operative process.

The mother liquor containing phosphoric acid and potassium dihydrogen phosphate may be recycled to the original reaction mixture.

The invention also provides a process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with aqueous hydrochloric acid to produce a reaction mixture comprising phosphoric acid, calcium phosphate and calcium chloride in solution; reacting said reaction mixture with further phosphate rock to form a suspension containing precipitated dicalcium phosphate and unreacted phosphate rock; adding alkaline material selected from the group consisting of limestone, lime, sodium hydroxide and sodium carbonate to the suspension to produce a slurry comprising insoluble dicalcium phosphate and unreacted phosphate rock in suspension in a solution of calcium chloride; separating off the calcium chloride in solution; reacting the resulting mixture comprising dicalcium phosphate and unreacted phosphate rock with a medium comprising potassium bisulphate, sulphuric acid and phosphoric acid to form a reaction mixture containing said potassium dihydrogen phosphate; controlling in said reaction mixture the weight percentages of hydrogen (other than in water) and of sulphate ion (in solution) relatively to phosphorus pentoxide to en-

sure precipitation of calcium sulphate in a readily separable state; and separating said calcium sulphate from said reaction mixture, whereby said potassium dihydrogen phosphate is recoverable from said reaction mixture.

In one embodiment of the invention, phosphate rock is reacted with aqueous hydrochloric acid to produce a reaction mixture comprising phosphoric acid, calcium phosphate and calcium chloride. This is reacted with further quantities of phosphate rock to precipitate dicalcium phosphate and limestone, lime or other alkaline material is added to produce a slurry comprising the insoluble dicalcium phosphate and unreacted phosphate rock in suspension in a solution of calcium chloride. The solids are separated and washed free from chloride. These reactions may be illustrated as follows:

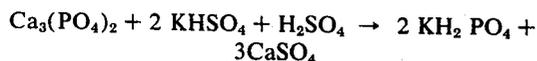


The resulting solids are reacted with a medium comprising potassium bisulphate and sulphuric acid, obtained by reaction of sulphuric acid on potassium chloride, and recycled phosphoric acid. The crystalline calcium sulphate produced can be filtered off from the mother liquor and the potassium dihydrogen phosphate product can be recovered from the mother liquor. Hydrochloric acid formed by the above reaction of sulphuric acid on potassium chloride may be used for the initial attack on the phosphate rock. The use of hydrochloric acid in this way contributes to the economics of the process.

In order to obtain calcium sulphate in a filterable form, high acid concentrations are necessary in the reaction slurry. This acid manifests itself in the crystallizing liquor and, under the conditions necessary for good yields, an addition product of potassium phosphate with phosphoric acid is formed $\text{KH}_2\text{PO}_4 \cdot \text{H}_3\text{PO}_4$. This material crystallizes from solution. It is found, that, if a water-miscible organic liquid such as methanol, ethanol, isopropanol or acetone is added to the liquor, potassium phosphate of good analysis is obtained in a good yield. The associated phosphoric acid remains in solution. The organic liquid is recovered in a still and returned to the process. Virtually all the impurities present in the solution, chiefly fluorine compounds, are precipitated with the product and the residual solution of phosphoric acid and potassium phosphate, after removal of the organic liquid is of high purity and can be used in the manufacture of other phosphates or returned to the process.

The attacking medium may be formed through the reaction of sulphuric acid on potassium chloride.

In the reaction between sulphuric acid and potassium chloride it has been found that the removal of the hydrochloric acid is a relatively easy matter if the reaction is carried out in the amounts required for the overall reaction but this is not so easily achieved if stoichiometric quantities are used. Thus, it is a feature of this embodiment of the invention to use excess acid which is subsequently reacted with phosphate rock. The second reaction between the phosphate rock and the acid slurry has been shown to proceed quantitatively and impure potassium phosphate has been isolated in yields up to 95 percent. These reactions may be illustrated as follows:



The hydrochloric acid produced as a by-product is a saleable commodity but may be converted to other desired materials or used for phosphoric acid production or dicalcium phosphate production or used intrinsically in the process as described.

Instead of forming the attacking medium by the reaction of sulphuric acid on potassium chloride, we may use potassium sulphate together with excess sulphuric acid but we prefer to use the reaction on potassium chloride since this is a readily available and economic starting material.

Formulations based on the potassium dihydrogen phosphate product of the process of the invention are as follows:

EXAMPLE 1

Product analysis 36% P_2O_5 36% K_2O	
Potassium phosphate	78.6%
Potassium chloride (60% K_2O)	21.4%

EXAMPLE 2

Product analysis 20% N 20% P_2O_5 20% K_2O	
Urea	44.5%
Potassium phosphate	43.7%
Potassium chloride (60% K_2O)	11.8%

EXAMPLE 3

A chloride free compound of analysis 27% N 13.5% P_2O_5 13.5% K_2O .	
Urea	60.0%
Potassium phosphate	29.5%
Potassium sulphate (50% K_2O)	10.5%

These materials may be made as granulates or may be prilled.

For a better understanding of the invention flow sheets four embodiments of the process according to the invention are shown on the accompanying drawings.

Flow sheet 1 relates to the treatment of the phosphate rock with a medium comprising sulphuric acid and phosphoric acids and potassium bisulphate produced from potassium chloride by sulphuric acid attack.

The apparatus comprises a reactor 1 for the phosphate rock attack followed by a calcium sulphate filter 2, an evaporator 3, a crystallizer 4, a separator and washer 5 and a dryer 6. Conduits 7 recycling mother liquor from the separator 5A to the reactor 1 and conduits 8 recycled from the washer 5B to the lower half 2A of the filter.

If hydrochloric acid is used intrinsically in the process and precipitation of the product is achieved by means of a water-soluble organic liquid, the apparatus comprises: reaction vessels for the rock attack, a filter for separating the reprecipitated phosphate, a reactor for the sulphate reaction with phosphate, a calcium sulphate filter, an evaporator, a precipitator, a separator and washer, and a dryer and distillation column for the recovery of the organic liquid.

A sulphate converter 9 with a potassium chloride feeder 10 and a sulphuric acid feeder 11 is provided to supply at 12 potassium bisulphate and sulphuric acid to

the reactor. Phosphate rock is fed directly to the reactor from a feeder 13.

The apparatus may be operated as follows:

Phosphate rock is digested in the reactor 1 by the acid medium comprising potassium bisulphate and sulphuric acid from the converter 9 and recycled mother liquor containing phosphoric acid from the separator 5A. The reactor product is fed at 14 to the filter section 2A as a suspension of crystalline calcium sulphate in a dilute solution of potassium dihydrogen phosphate in phosphoric acid. The calcium sulphate crystals are separated off at 24 in the section 2A and the liquid medium is concentrated in the evaporator 3 to approximately 40 percent weight potassium dihydrogen phosphate. Potassium dihydrogen phosphate crystals are then formed in the crystallizer 4 and the resulting suspension is fed to the separator and washer 5A, 5B. The product crystals are finally dried at 6 and form a product 20.

The gaseous hydrogen chloride from the converter is fed to a scrubber 15 in which it is absorbed to form a hydrochloric acid solution which is a by-product 16 of the process. Water is fed to the filter wash section 2B at 17 and to the washer 5B at 18. Heat is supplied to the drier 6 at 19. The evaporator 3 is vented to atmosphere at 21 through a scrubber 22. A mixture of potassium dihydrogen phosphate and dilute phosphoric acid is fed at 23 from the wash section 2B to the reactor 1.

Flow sheet 2 illustrates the alternative of the recovered hydrochloric acid being used in the process. Phosphate rock fed at 25 is digested in reaction vessels 1A with hydrochloric acid solution from the absorber 15A fed at 16A. The resulting phosphoric acid is converted to insoluble dicalcium phosphate in reactor 1B by the addition at 26 of the remainder of the phosphate required in the reaction and limestone from a feeder 27 entering reactor 1C at 28. The solids are separated on a filter 29 and washed free of chloride. They are then reacted in the reactor 1 with an acid solution of potassium sulphate from the sulphate converter 9 and recycled liquor containing phosphoric acid from the separator washer 5. A portion of the phosphate rock is fed at 30 directly to the reactor 1. Waste calcium chloride leaves the filter 29 at 31.

Flow sheet 3 illustrates a further alternative, using an organic solvent miscible with water. Potassium dihydrogen phosphate is precipitated in the precipitator 4A by the addition at 33 of organic liquid from a feeder 34. The resulting suspension is fed to the separator and washer 5. The crystals are separated and dried and are then in a saleable form. The mother liquor containing water, phosphoric acid, residual potassium phosphate and organic precipitant is fed to a distillation column 35 where the organic liquid is recovered and the phosphoric acid and potassium phosphate separated can be sent back to the process as shown at 36 or used for the manufacture of pure phosphates. The feeder 34 is replenished from a supply 32.

Flow sheet 4 shows the use of the organic solvent in an embodiment according to flow sheet 1.

This invention is illustrated by the following examples:

EXAMPLE 1

352 parts by weight muriate of potash (60% K_2O) and 958 parts by weight of 96% H_2SO_4 were reacted together and the HCl gas evolved was removed. The sul-

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phate solution was reacted with 1,000 parts of Morocco rock (33.1/3% P_2O_5) and recycled phosphate liquors from the phosphate still and from the calcium sulphate filter. In the reaction mixture, the weight percentage of hydrogen relative to P_2O_5 was maintained at 3.6 percent and the weight percentage of sulphate ion to P_2O_5 was maintained at 6.62 percent. The calcium sulphate formed was filtered off. Water was evaporated from the filtrate to give a solution containing 40% P_2O_5 by weight. 715 parts of 95 percent methanol in water were added to the phosphate liquor in a crystallizer and 674 parts of solid of analysis 19.9% P, 25% K were removed. Methanol was stripped from the remaining liquid which was returned to the reactor.

EXAMPLE 2

352 parts by weight of muriate of potash (60% K_2O) and 863 parts by weight of 96% H_2SO_4 were reacted together to produce a sulphate liquor (I). The HCl gas evolved was absorbed in 800 parts water and the solution reacted with 1,000 parts phosphate rock 33.1/3% P_2O_5 . After reaction, 133 parts limestone were added. Solids were filtered off and washed substantially free of chloride. The solids were reacted in the reactor with the sulphate liquor (I) and return phosphate liquors from the still and from the calcium sulphate filter, and conditions were maintained in the reactor as in Example 1. Calcium sulphate was filtered from the reactor mixture and the liquor treated as in Example 1.

EXAMPLE 3

This was as in Example 1 but evaporated liquor was treated first with 240 parts 95 percent Methanol in water to give 445 parts solids of analysis 18.12% P, 22.86%K. The solids were removed and 475 parts 95% Methanol in water were added to the remaining liquor to give 233 parts solids of analysis 22.9% P, 28.6%K.

EXAMPLE 4

This was as in Example 2 but evaporated liquor was treated as in Example 3 to give the same results as in Example 3.

EXAMPLE 5

352 parts of muriate of potash (60% K_2O) and 1,724 parts of 96% H_2SO_4 were reacted together and the HCl gas evolved was removed. The sulphate solution was reacted with 1,841 parts Morocco rock (33.1/3% P_2O_5). The conditions in the reactor were maintained by means of recycled phosphate liquors from the still and calcium sulphate filter so that the hydrogen ion concentration relative to P_2O_5 was 3.6 percent and the sulphate ion concentration relative to P_2O_5 was 6.6 percent. The calcium sulphate formed was filtered off and the phosphate solution was evaporated to 40% P_2O_5 . 603 parts of 95 percent Methanol in water were added to the phosphate liquor in a crystallizer and 568 parts of solid of analysis 19.9% P, 24.8%K were removed. Methanol was stripped from the remaining liquor which was removed from the system. The liquor contained 34.75% P_2O_5 and 3.54% K_2O .

EXAMPLE 6

This was as in Example 5 but the liquor remaining after the removal of PK solids was treated with 2414 parts methanol to give 86 parts of solids of analysis 22.8%P, 28.8%K, which were removed. Methanol was

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stripped from the remaining liquor which contained 0.27% K_2O and 34% P_2O_5 and was substantially free from Fe, Ca, F and S.

EXAMPLE 7

This was as in Example 5 but the HCl gas was used as in Example 2 and the 96% H_2SO_4 requirement was reduced to 1,629 parts.

EXAMPLE 8

This was as in Example 7 but the liquor remaining after the removal of P,K solids was treated as in Example 6 to give the same results as in Example 6.

EXAMPLE 9

Ground Morocco rock 5 (33.1/3% P_2O_5) sulphate of potash and 96 percent sulphuric acid were reacted at 65°/70° C. with recycle phosphate liquors from the calcium sulphate filter and still. The ratio of rock P_2O_5 to recycle P_2O_5 was 1:3.4 and the percentage of water in the reaction mixture was 45.1 percent. The weight percentage of hydrogen relative to P_2O_5 was maintained at 3.8 percent and the weight percentage of sulphate ion to P_2O_5 was maintained at 6.1 percent. The calcium sulphate produced was in the dihydrate form.

EXAMPLE 10

This was as in Example 9 but the reaction temperature was 105°/110° C. and the percentage of water in the reaction mixture was 22.7 percent. The calcium sulphate produced was mainly in the hemihydrate form.

Although the invention has been particularly described with reference to the formation of potassium dihydrogen phosphate, it will be appreciated that it can be adapted without difficulty to the production of sodium and ammonium phosphate. Thus, monoammonium phosphate can be made from ammonium sulphate, sulphuric acid and phosphate by a similar process to that described above. In the case of sodium phosphate, the source of sodium is sodium chloride.

I claim:

1. A process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with an aqueous medium containing potassium bisulphate, sulphuric acid and phosphoric acid to form a liquid reaction mixture containing potassium dihydrogen phosphate; controlling in said liquid reaction mixture the weight percentage of hydrogen ions, other than those present in water, relative to phosphorus pentoxide and the weight percentage of sulphate ions in solution relative to phosphorus pentoxide to ensure precipitation of calcium sulphate in a readily separable state; separating precipitated calcium sulphate from the liquid reaction mixture to provide an aqueous solution containing potassium dihydrogen phosphate; recovering potassium dihydrogen phosphate from said aqueous solution; and recycling to said aqueous medium a proportion of the remaining potassium dihydrogen phosphate solution to constitute part of said aqueous medium for controlling at least in part the weight percentages.

2. A process according to claim 1 wherein said weight percentage of hydrogen ions to phosphorus pentoxide is greater than about 2 percent and said weight percentage of sulphate ions to phosphorus pentoxide is greater than about 3 percent.

3. A process according to claim 2 wherein said weight percentage of hydrogen ions to phosphorus pentoxide is greater than about 3 percent and said weight percentage of sulphate ions to phosphorus pentoxide is greater than about 5 percent.

4. A process according to claim 3 wherein said weight percentage of hydrogen ions to phosphorus pentoxide is about 4 percent and said weight percentage of sulphate ions to phosphorus pentoxide is about 6 percent to about 7 percent.

5. A process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with hydrochloric acid to produce an aqueous mixture containing phosphoric acid, calcium phosphate and calcium chloride in solution; reacting said aqueous mixture with further phosphate rock to form a suspension containing precipitated dicalcium phosphate and unreacted phosphate rock; adding alkaline material selected from the group consisting of limestone, lime, magnesium hydroxide and magnesium carbonate to the suspension to produce a slurry containing insoluble dicalcium phosphate and unreacted phosphate rock in suspension in a solution of calcium chloride; separating off the calcium chloride in solution; reacting the resulting mixture containing dicalcium phosphate and unreacted phosphate rock with a medium containing potassium bisulphate, sulphuric acid and phosphoric acid to provide a liquid reaction mixture containing said potassium dihydrogen phosphate; controlling in said reaction mixture the weight percentage of hydrogen ions other than those present in water relative to phosphorus pentoxide and the weight percentage of sulphate ions in solution relative to phosphorus pentoxide to ensure precipitation of calcium sulphate in a readily separable state; and separating precipitated calcium sulphate from said reaction mixture to provide an aqueous solution containing said potassium dihydrogen phosphate; recovering potassium dihydrogen phosphate from said aqueous solution; and recycling to said aqueous medium a proportion of the remaining potassium dihydrogen phosphate solution to constitute part of said aqueous medium for controlling at least in part the weight percentages.

6. A process according to claim 5 in which further phosphate rock is added to said reaction mixture containing dicalcium phosphate and unreacted phosphate rock for reaction with said medium containing potassium bisulphate, sulphuric acid and phosphoric acid.

7. A process according to claim 5 in which said reaction mixture of phosphoric acid, calcium phosphate and calcium chloride is obtained by reacting gaseous hydrogen chloride with a mixture containing phosphate rock and water.

8. A process according to claim 7 in which said hydrogen chloride is obtained as a by-product of sulphuric acid attack on potassium chloride to form said potassium bisulphate and sulphuric acid components of said medium for reaction with said phosphate rock to form said potassium dihydrogen phosphate.

9. A process according to claim 8 in which said hydrogen chloride is absorbed in water.

10. A process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with an aqueous medium containing potassium bisulphate, sulphuric acid and phosphoric acid to form a liquid reaction mixture containing potassium dihydrogen phosphate; controlling in said liquid

reaction mixture the weight percentage of hydrogen ions, other than those present in water, relative to phosphorus pentoxide and the weight percentage of sulphate ions in solution relative to phosphorus pentoxide to ensure precipitation of calcium sulphate in a readily separable state; separating precipitated calcium sulphate from the liquid reaction mixture to provide an aqueous solution containing potassium dihydrogen phosphate; precipitating potassium dihydrogen phosphate from the aqueous phosphoric acid solution constituting said liquid reaction mixture, after the separation therefrom of said calcium sulphate, by the addition of a water miscible organic solvent to said aqueous solution; and separating the resulting solid potassium dihydrogen phosphate product from a mother liquor containing in solution phosphoric acid, potassium dihydrogen phosphate and organic solvent.

11. A process according to claim 1 in which at least some of said phosphoric acid in said reaction mixture is supplied by the attack on phosphate rock of at least one from the group consisting of sulphuric acid, hydrochloric acid and potassium bisulphate.

12. A process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with an aqueous medium comprising potassium bisulphate, sulphuric acid and phosphoric acid to form a liquid reaction mixture containing potassium dihydrogen phosphate; controlling in said reaction mixture the weight percentage of hydrogen ions, other than those present in water, relative to phosphorus pentoxide and the weight percentage of sulphate ions in solution relative to phosphorus pentoxide to have a H/P_2O_5 weight percentage greater than about 2 percent and a SO_4/P_2O_5 weight percentage greater than about 3 percent; separating precipitated calcium sulphate from the liquid reaction mixture to provide an aqueous solution containing phosphoric acid and potassium dihydrogen phosphate; precipitating and recovering solid potassium dihydrogen phosphate from said solution thereof; and recycling to said aqueous medium a proportion of potassium dihydrogen phosphate and phosphoric acid solution to constitute part of said aqueous medium for controlling at least in part the weight percentages.

13. A process for the production of potassium dihydrogen phosphate comprising the steps of reacting phosphate rock with an aqueous medium containing potassium bisulphate, sulphuric acid and phosphoric acid to form a liquid reaction mixture containing potassium dihydrogen phosphate; controlling in said liquid reaction mixture the weight percentage of hydrogen ions, other than those present in water, relative to phosphorus pentoxide and the weight percentage of sulphate ions in solution relative to phosphorus pentoxide to ensure precipitation of calcium sulphate in a readily separable state; separating precipitated calcium sulphate from the liquid reaction mixture to provide an aqueous solution containing potassium dihydrogen phosphate; recovering potassium dihydrogen phosphate from said aqueous solution by precipitating solid potassium dihydrogen phosphate from said aqueous solution by the addition of a water miscible organic solvent to said aqueous solution to form a suspension of solid potassium dihydrogen phosphate in a mother liquor containing in solution phosphoric acid, potassium dihydrogen phosphate and organic solvent; and sepa-

rating said solid potassium dihydrogen phosphate from said mother liquor.

14. A process according to claim 13 and further comprising the steps of distilling said mother liquor to recover said organic solvent therefrom; recycling said organic solvent to the potassium dihydrogen phosphate precipitation stage; and at least partly removing as a by-product the remaining solution containing an aqueous solution of phosphoric acid and potassium dihydrogen phosphate.

15. The process according to claim 13 further comprising the steps of distilling said mother liquor to recover said organic solvent; recycling said organic solvent to the potassium dihydrogen phosphate precipitation stage; and recycling a proportion of the remaining aqueous solution of phosphoric acid and potassium dihydrogen phosphate to said reaction mixture obtained by the reaction of phosphate rock with said aqueous medium containing potassium bisulphate, sulphuric acid and phosphoric acid.

16. The process according to claim 13 further comprising the step of separating at least partly as a by-product which is substantially free of iron, calcium, fluorine and sulphur, a remaining solution comprising

phosphoric acid and potassium dihydrogen phosphate.

17. A process according to claim 1 in which the step of recovering said potassium dihydrogen phosphate from said aqueous solution includes the step of subjecting said aqueous solution to crystallization of said potassium dihydrogen phosphate.

18. A process according to claim 17 in which said aqueous solution is subjected to evaporation prior to said crystallization of said potassium dihydrogen phosphate.

19. A process according to claim 1 and further comprising the step of granulating said potassium dihydrogen phosphate.

20. A process according to claim 1 and further comprising the step of prilling said potassium dihydrogen phosphate.

21. A process according to claim 1 and further comprising the step of formulating at least part of said potassium dihydrogen phosphate as a fertilizer material.

22. A process according to claim 1 in which at least part of said potassium dihydrogen phosphate product is recovered in a form substantially free of iron, calcium, fluorine and sulphur.

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